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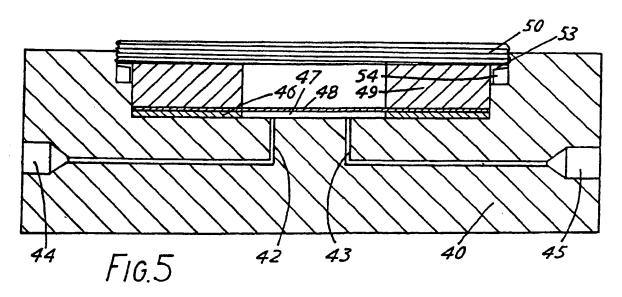
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(54) Gas absorbing cell for gas analyser

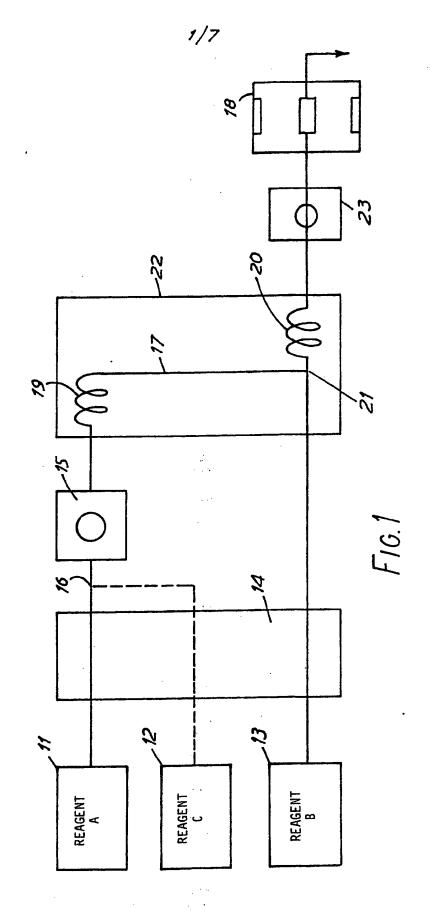
(57) A gas analyser comprises a gas absorbing cell 15 having a chamber 47 for liquid reagent separated from a region 52 containing sample gas by a gas-permeable 48 membrane. The liquid reagent undergoes a colour change when the gas to be detected is present. The chamber 47 has an inlet port 42 connected to a supply of liquid reagent 11 and an outlet port connected to a photometric sensing cell (18, fig. 6) which detects the colour changes in the liquid reagent when the gas to be detected is present. Low liquid flow rates through the two cells are obtained by means of a flexible container for the liquid reagent which is compressed by plate or by external air pressure (figs. 8 and 9).



A least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

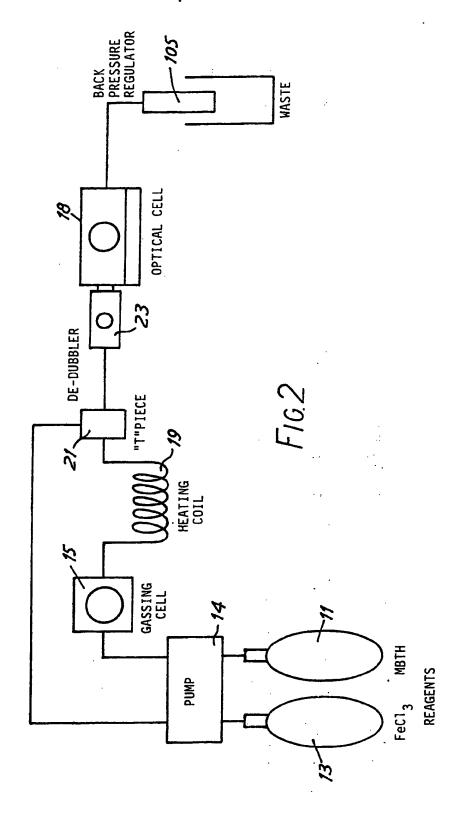
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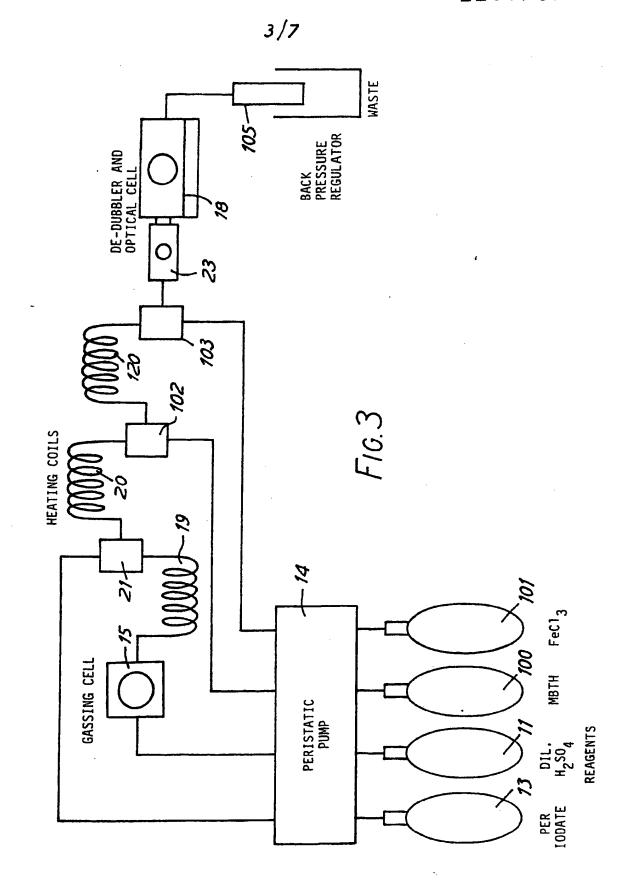


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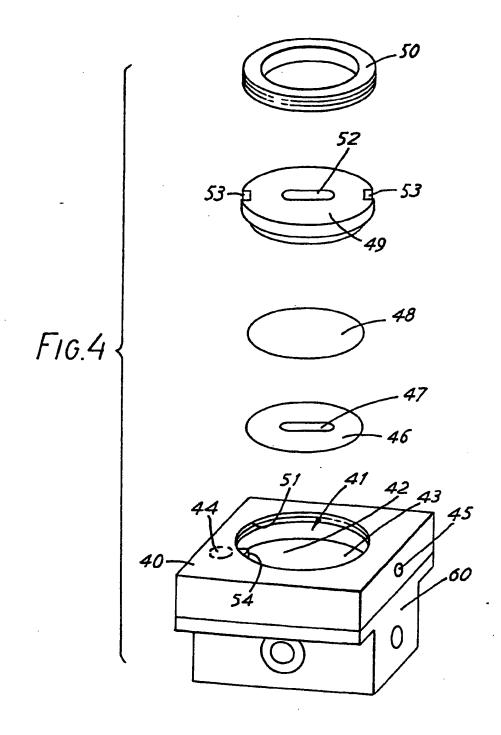
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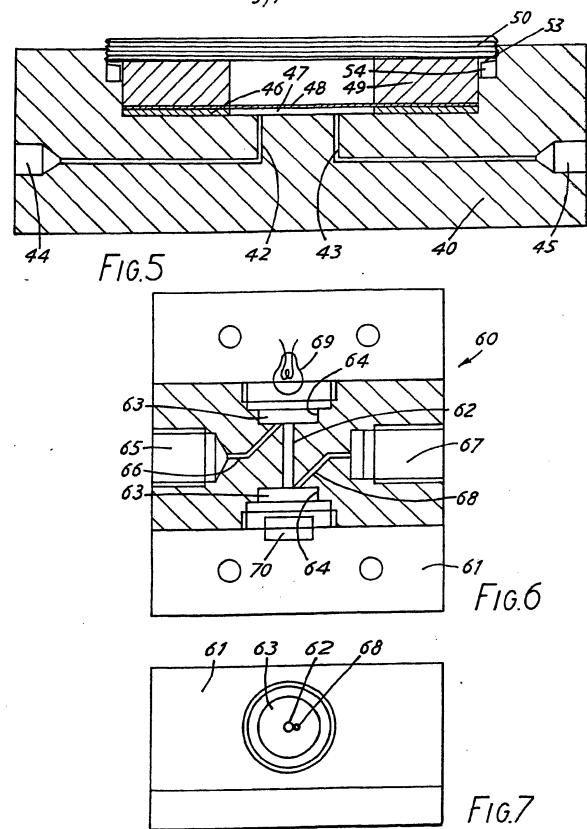
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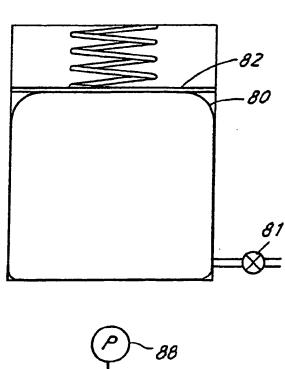
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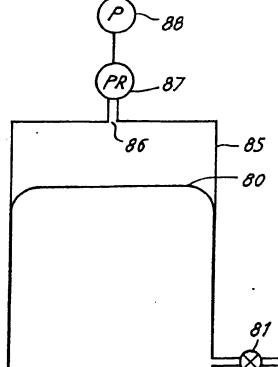
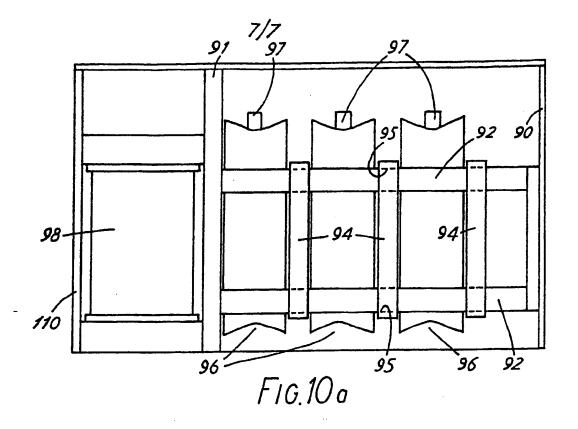
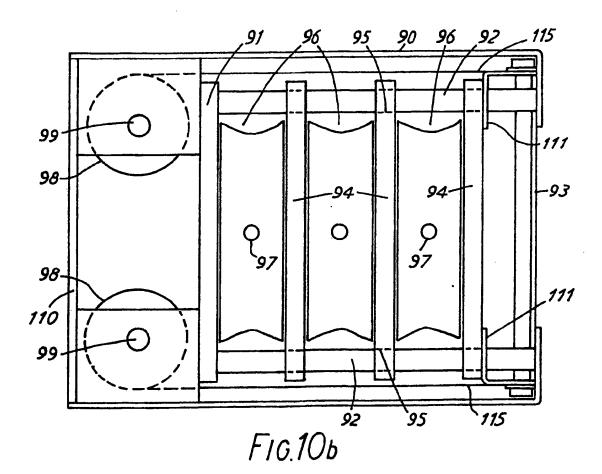


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GAS ANALYSER

The present invention relates to the detection of gaseous compounds. It is concerned especially, but not exclusively, with the detection of gaseous compounds using colorimetric techniques. It also relates to an optical cell for detecting colour changes in liquid reagents and to a liquid pump.

The detection (normally in ambient air) of toxic and carcinogenic gaseous compounds, is important for health and safety in both the working and living environment. Usually such compounds must be detected at concentrations of a few parts per million (ppm) by volume, or less. The levels of allowable concentrations are continually being lowered as the chronic effects of chemicals become known. Consequently the sensitivity of gas detecting apparatus must be improved.

Colorimetric methods of detecting gases depend on the selective and sensitive colour producing reactions between the particular compound to be detected and suitable reagents. These reactions usually take place in solution. The colours produced are measured photometrically. These colorimetric methods usually depend on having a pumped, metered sample of gas in direct contact with the reagent solutions, in some form of gas bubbler. Commercial equipment is available for performing such analyses. This equipment generally uses flow rates of tens of millilitres per hour of liquid reagent so that several litres of reagent are used in the course of one week of continuous monitoring. Other gas detecting techniques which rely on the absorbtion or reaction of the gases to be detected by liquid reagents suffer from similar problems.

The present invention aims at overcoming the problems of size, and cost of reagent associated with the use of conventional moving liquid gas analysers.

According to the present invention there is provided a gas analyser comprising a gas absorbing cell having a chamber for liquid reagent separated from a region containing sample gas by a gas permeable membrane, the chamber having an inlet port for connection to a supply of liquid reagent and an outlet port connected to sensing apparatus for detecting a change in the liquid reagent due

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to the presence of the gas to be detected, the effective surface area of the gas permeable membrane being large compared with the volume of the liquid chamber.

Preferably the ratio of the effective area of the membrane to the volume of the liquid chamber is 5mm⁻¹ or more. Typically the ratio will be in the range of 5 to 20mm⁻¹, for example 10mm⁻¹. The liquid chamber may have a thickness substantially smaller than its length or width and the membrane may form one of the major walls of the chamber. The thickness of the chamber may be .1mm or less.

The analyser according to the invention enables a sample of a gaseous compound from, for example, ambient air to be collected by diffusion through the gas permeable membrane into the liquid reagent in the chamber, which may be stationary or moving. The gas diffusion cell should be so constructed as to give the best practicable surface/volume ratio compatible with the volume of the absorbing cell, and to allow maximum contact between the gas and the liquid reagent.

The gas thus collected in the liquid reagent either reacts directly with the collecting reagent, or is mixed subsequently with other reagents, to produce, for example, a coloured compound which can be detected photometrically. Alternatively, once the gas is trapped in the liquid medium it can be analysed or monitored using other detection methods such as conductivity, ion selective electrodes, electrochemical reaction, spectrophotometry, or even by injection into suitable chromatographic apparatus.

The apparatus of the present invention enables very low liquid reagent flow rate through the gas absorption cell to be used, typically in the range 5 to $250\,\nu\,l$ per minute and preferably in the range 5 to $50\,\nu\,l$ per minute. Such flow rates give a weekly usage (168 hrs continuous running) of 50 to 500 mls of reagents. Thus the present invention can be operated using liquid flow rates that are at least an order of magnitude lower than the known gas bubbler technique.

In a preferred embodiment the sensing apparatus is an optical sensor, preferably a photometer.

The output from the photometer may be processed electronically to provide an indicated value of the ambient gas concentration. The

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electronic circuitry may be constructed so as to provide an alarm signal when the level of the gas detected exceeds a predetermined value.

Another embodiment of the invention is especially designed for use in a hazardous environment. The conventional gas analysers used in such environments have their electrical circuitry contained within a robust flameproof enclosure or, if possible, operate within the power constraints of intrinsically safe electrical designs. The design complexity and added cost of manufacturing such conventional instruments to comply with officially certified designs is avoided with the present invention if the gas absorbing cell and optical cell are located in the hazardous area together with a non-electric liquid pumping means (for example an air or spring pressure driven pump with an orifice for controlling flow) and fibre optic guides are used to link the optical cell to the measuring photometer located in a designated safe area.

The invention also provides a novel optical cell and a novel pump which may be used independently of the gas absorbing cell.

According to the present invention in a second aspect there is provided an optical cell comprising a body with a transverse bore closed at its ends by windows, an inlet connected to the bore adjacent one of its ends and an outlet connected to the bore adjacent the other of its ends, the inlet being connected to a source of fluid whereby fluid passes from the inlet to the outlet through the bore, a light source mounted outside one window and a photo detector being mounted outside the other window so that the photo detector detects light from the light source passing through the liquid in the bore.

According to the present invention in a third aspect there is provided a liquid pump comprising a flexible container containing liquid to be pumped, a pulsed valve in an outlet connected to the flexible container and means for applying pressure to the flexible container.

Embodiments of the invention will now be described, by way of example, with reference to the accompanying drawings, of which:-

Fig. 1 shows a schematic arrangement for a colorimetric gas detecting system in accordance with the invention;

Fig. 2 shows a schematic arrangement of a colorimetric gas detecting system in accordance with the invention for detecting formaldelyde;

Fig. 3 shows a schematic arrangement of a colorimetric gas detecting system in accordance with the invention for detecting ethylene oxide;

Fig. 4 shows and exploded view of the gas diffusion cell of the system of Fig. 1, 2 or 3;

Fig. 5 shows a cross-section of the cell of Fig. 4;

Fig. 6 shows the optical cell of the system of Fig. 1, 2 or 3;

Fig. 7 shows a side elevation of the cell of Fig. 6;

Fig. 8 shows a pump which may be used in the system of Fig. 1, 2 or 3;

Fig. 9 shows an alternative form of pump which may be used; and Fig. 10 shows a further alternative form of pump.

Referring to Fig. 1, a colorimetric gas analyser comprises reservoirs 11, 12 and 13 for three liquid reagents A, B and C which produce a colour change reaction when a particular gas is present. A pump 14 delivers liquid reagents A and C from the reservoirs 11 and 12 to a gas absorbing cell 15, the reagents being mixed in a T-piece mixer 16 before entry into the cell 15.

In the gas absorbing cell sample gas is dissolved in the liquid reagent mixture. The reagent mixture passes through a delivery pipe 17 to an optical cell 18. On its way to the optical cell the reagents may pass through delay loops 19 and 20 which increase the length of the delivery pipe and thus increase the time taken by the liquid mixture to reach the optical cell. This allows time for the colour change reaction to take place. Reagent B is pumped from the reservoir by the pump 14 and mixed with the mixture from the gas absorbing cell 15 at a T-piece 21, located between the delay loops 19 and 20. The delay loops 19 and 20 may be heated by a heat exchanger 22 to accelerate the colour change reaction.

Before entering the optical cell 18 the liquids are passed through a de-bubbling cell 23 to remove bubbles which would otherwise interfere with the working of the optical cell. The de-bubbling cell 23 comprises a small channel with an area covered by a gas-permeable membrane to allow gas bubbles to escape from the

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liquid in the system. After passing through the optical cell the liquids are passed to waste at 24.

The reagents used will depend on the gas to be detected. For some gases it will not be necessary to use a three reagent system and therefore some of the reservoirs, pipework and T-pieces may be omitted. The dimensions of the delay loops and the heating requirements will also depend on the characteristics of the colour change reaction.

For example, to detect ammonia gas, a single reagent m-cresol purple indicator may be used which undergoes a simple colour change from yellow to purple in the presence of ammonia.

To detect formaldehyde a modification of the MBTH method described in "Colorimetric Chemical Analytical Methods" by L.C.

Thomas and G.J. Chamberlin at page 496 may be used. Fig. 2 shows a schematic diagram of an analyser for carrying out this method. The sample gas is mixed with a solution of MBTH (3 methylbenzothiazol- 2 one hydrazone hydrochloride) from the reservoir 11 in the gas absorbing cell 15. This solution is heated to 70°C in the delay loop 19 before being mixed with an aqueous solution of hydrochloric acid and ferric chloride from the reservoir 13 at the mixer piece 21. If formaldehyde is present in the sample gas absorbed at the cell 15 the solution changes from colourless to blue.

To detect ethylene oxide, the method described in a conference paper by Kring, Henry, McGibney and Ansul of EI DuPont de Nemours & Co. entitled "New Passive Colorimetric Air Monitoring Badges for Sampling Ethylene Oxide in Air - DuPont Protek Series II" at the American Industrial Hygiene Conference, Cincinatti, Ohio, June 1982 may be used. Fig. 3 shows a schematic diagram of an analyser for carrying out this method. The sample gas is mixed with dilute aqueous sulphuric acid (0.05 N) from the reservoir 11 in the gas cell 15. The solution is then heated to 80°C in the delay loop 19 to hydrolyse any ethylene oxide present to ethylene glycol. This solution is then mixed in the T-piece 21 with an aqueous solution of tri sodium dihydrogen orthoperiodate from the reservoir 13 and maintained at 80°C in the heated delay loop 20 to oxidise the ethylene glycol to formaldehyde. The formaldehyde is then detected as described above by mixing in the T-piece 102 with the aqueous

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MBTH from the reservoir 100 and maintaining the solutions at 80°C in the delay loop 120. The solution is then mixed in the T-piece 103 with aqueous HCI/FeCl₃ from the reservoir 101. The colour change is colourless to blue.

Other techniques are known for detecting hazardous gases, see for example "Colorimetric and Fluorimetric Analysis of Organic Compounds and Drugs" by M. Pesez and J. Bartos and the book mentioned above.

Figs. 4 and 5 show the gas absorbing cell 15. The cell comprises a cell body 40 machined from a suitable plastic, for example PVC or PTFE, with a circular cavity 41 in its upper surface. Typically the body will measure 35mm and 35mm x 22mm high and the cavity will be approximately 25mm in diameter. Inlet and outlet ports 42 and 43 are drilled in the floor of the cavity 41 and intersect inlet and outlet conduits 44 and 45.

A spacer 46 has an oblong aperture 47 cut through it and is placed on the floor of the cavity with the inlet and outlet ports in register with the cut out aperture 47. A gas permeable membrane 48 is placed over the space 46 and held in place by a pressure plate 49 and a screw threaded locking ring 50 which engages screw threads 51 on the peripheral wall of the cavity 41. The aperture 47 thus forms a chamber which is bounded on one side by the gas permeable membrane 48. A slot 52 in the pressure plate 49 corresponds in size with the cut out aperture 47 and provides access for the ambient gas to the gas permeably membrane 48. Notches 53 in the edge of the pressure plate engage lugs on the peripheral wall of the cavity 41 to ensure that the slot 52 remains in register with the cut-out aperture 47 in the spacer 46.

In use the liquid reagent is pumped into the chamber formed by the aperture 47 through the inlet conduit 44 and the inlet port 42 and emerges through the outlet port 43 and the outlet conduit 45. Whilst the liquid is in the chamber 47 gases in the ambient air diffuse through the membrane and dissolve in the liquid in the chamber.

The dimensions of the chamber in the horizontal direction are much greater than the thickness of the chamber in the vertical direction which is determined by the thickness of the cell spacer

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46. The effective surface area of the gas permeable membrane 48, that is the area exposed to the chamber 47 and the ambient air, is therefore large compared with the volume of the chamber. This construction ensures that the rate at which gas is absorbed by the liquid in the cell is high with the result that a high concentration of gas in the liquid can be achieved in a short time.

Typically the chamber 47 may be 10mm long, 5mm width and 0.1mm thick giving a ratio of effective surface area of membrane to cell volume of 10mm⁻¹. The thinner the cell spacer 46 the higher the ratio of surface area to volume. Useable cells having ratios of between 5 to 20mm⁻¹ have been constructed with a value of 10mm⁻¹ being typical.

The gas permeable membrane 48 may be made in a variety of plastics material, for example polytetrafluoroethylene (PTFE), mylon, polyvinylchloride (PVC), polypropylene, polysulfone, or polyethylene. The thickness of the membrane is typically 0.05 to 0.1mm with a range of individual pore sizes. The membrane is preferably reinforced with a polyester mesh to give added strength over the gassing area. By using a reinforced membrane the tendency for the membrane to distort under the pressure of the liquid in the liquid chamber is reduced.

The liquid can be pumped slowly through the cell allowing the level of dissolved gas in the liquid to build up giving higher sensitivities for the detection of low concentration hazardous gas in the ambient air. The gas diffusion cell with its low volume and high gas sampling rate allows the use of the very low flow rates of reagent. The use of such low flow rates with acceptable response times is not possible with direct gas/liquid contact bubblers.

The use of the gas diffusion cell simplifies and in many cases eliminates the need for, the removal of bubbles from the liquid system. Such trapped bubbles cause instability in the detected optical signals. The de-bubbling cell 23 may therefore be omitted in certain applications.

Controlling the rate or flow of liquid in the cell is equivalent to changing the gas sampling flow rate in a conventional bubbler and may be used to set the concentration range of the apparatus, whilst at the same time maintaining the low flow rate of

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liquid reagent.

Figs. 6 and 7 shows the construction of the optical cell. This may be mounted on the same body 40 of the gas absorbing cell 15 as indicated at 60 in Fig. 4.

The optical cell 18 comprises a body 61 of a suitable plastic with a transverse bore 62 which forms the optical path. Glass or quartz windows 63 are mounted in counter bores 64 at the ends of the bore 64. A liquid inlet port 65 communicates with one end of the bore 62 through a conduit 66 in the body 51 and a liquid outlet port 67 communicates with the other end of the bore 62 through a conduit 68.

A light source 69 is mounted outside one of the window 63 and a photo detector 70 is mounted outside the other window 63 so that light from the source 69 passes axially through the sample of liquid in the bore and falls on the detector 70.

The pump 14 pumps the liquid reagents through the gas absorbing cell 15 and the optical cell 18. The liquid passes in through the liquid inlet port 65, the conduit 66, along the bore 62 and out through the conduit 68 and the outlet port 67.

The light source 69 may comprise a light-emitting diode and may be pulsed to conserve electricity. The light source may emit green, red, infrared or ultraviolet light. The photo detector 70 may be a photo diode and may be arranged to respond to the variation in the total intensity of radiation falling on it or shifts in the intensity at a particular wavelength, due to variations in the attenuation of the light passing through the liquid in the bore 62 as the colour change occurs. The particular change to be detected will depend on the colorimetric change that is to be observed.

The photo detector 70 is connected in electronic circuitry which can be of conventional construction, to produce the desired response when a colour change is detected.

Because of the low volume of the liquid path through the optical cell, the cell enables the system to achieve great sensitivity with low volumes of liquid used. Typically the optical cell has a volume of the order of 2-100 µl, and preferably in the range 2-20 µl. Because of the low liquid flow rates used it has been necessary to reduce the possibility of bubble formation in the optical cells by careful design of the flowing liquid path. In

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particular it has been found advantageous to ensure liquid flow into and out of the optical cell, across the face of the optical windows of the cell. This is achieved by placing the outlet and inlet ends of the conduits 66 and 68 alongside the viewed volume of the cell, that is alongside the bore 62, at the plane of the glass window (see Figure 7).

Bubble formation in the system may also be reduced in two ways. Firstly a degassing membrane covered cell 23 is included in the liquid system just prior to the optical cell, and secondly a method of maintaining a positive pressure in the liquid system is fitted. This can be either a simple restrictive element e.g. a length of narrow bore tubing or a spring loaded valve located downstream of the optical cell 18. The latter element reduces the possibility of blockage by particulates in the flowing liquid. Such an element is indicated at 105 in Figs. 2 and 3.

The optical cell can be constructed as an integral part of the gas absorption cell if the colour producing reaction is rapid enough, otherwise the cell is separately constructed.

The introduction of components such as the heating coils and debubbling cell between the gas absorbing cell and the optical cell does of course affect the overall response time of the system.

For the fastest response from a single reagent system, the dead volume between the gas absorbing cell 15 and the optical cell 18 must be as small as possible. For example with a gas cell volume of 571 and liquid flow rate of 1071/min, a dead volume of 271 represents a delay time of 12 seconds. With an optical cell volume of 10%1, 90% response requires at least 1.5 minutes. To achieve the minimum response time a gas cell could be constructed with direct viewing of the liquid behind the gas permeable membrane. However with more complex chemistries, with built in delays for reagent heating, time for chemical reaction etc., response times will vary depending on total volumes and combined flow rates. The actual response time may be determined by what is acceptable in a particular application. For example NH3 gas can be detected in the simple single reagent system described above with a response time of less than 30 seconds, whereas formaldehyde can be detected using the more complex two reagent system described above with reference to

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Fig. 2 with a response time of four minutes.

Iow liquid flow rates are conventionally achieved using peristaltic or piston pumps. These methods can be used in the invention. Alternatively the liquid pumping system shown in Fig. 8, 9 or 10 may be used.

Referring to Fig. 8, pressure is applied to a flexible container 80 containing the liquid reagent placed in a rigid housing 85. A pulsed miniature valve 81 in an outlet pipe connected to the container 80 releases small quantities of liquid to give the low flow rates required. Pulse rates of 0.5 to 20 Hz are used with 1 Hz being typical. The ON/OFF duty cycle of the valve is varied within this pulse rate to finely control the liquid flow rate.

In fig. 8 the pressure is applied to the flexible bag 80 by means of a plate 82 which can move up and down in the housing 85 above the bag 80. The plate 82 is forced downwardly by means of a compression spring 83 acting between the top wall of the housing and the plate 82.

Fig. 9 shows a modification of the arrangement of Fig. 8 in which the pressure is applied to the flexible bag 80 by air pressure. The housing 85 which contains the bag 80 is air-tight. An inlet 86 is located in the top wall of the housing and is connected via a pressure regulator 87 outside the housing to a container of compressed air 88. The pressure regulator 87 ensures that the air in the housing is at constant pressure so that a constant pressure is applied to the bag 80. Liquid is released from the bag by a pulsed control valve 81 in the same manner as described in relation to Fig. 8.

In a typical application it will be necessary to control several reagent streams which mix together in order to produce the required colorimetric reaction with the absorbed gas. In such cases several such liquid pumps are employed.

Figs. 10a and 10b show side elevation and plan of a liquid pump capable of pumping up to three different reagents simultaneously, that may be used in the analysers of figs. 1 or 2 or with modification to include an extra container for a fourth reagent in the analyser of fig. 3.

A housing 90 has a vertical partition wall 91. Four parallel

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guide rails 92 are mounted between the partition wall 91 and an end wall 93 of the housing. Three plates 94 have holes 95 at their four corners and are mounted on the guide rails 92 with the rails passing through the holes 95. The plates are thus mounted parallel to one another and to the partition wall and capable of sliding along the rails.

Flexible containers 96 for the liquid reagents are placed between adjacent pairs of plates 94 and between the partition wall 91 and the adjacent plate 94. Each container has an outlet 97 connected to a pulsed control valve (not shown).

Two coiled constant tension springs 98 are mounted on vertical spindles 99 in the space between the partition wall 91 and the other end wall 110 of the housing. The ends 115 of the springs are pulled out and pass either side of the plate and guide rail assembly and are fixed to brackets 111 on the plate 94 furthest from the partition wall 91. As the coil springs 98 try to coil themselves more tightly around the spindles 99 they exert a constant tension force on the ends 100 urging the end plate 94 towards the left as viewed in Figs. 10a and 10b and thus squeezing the containers 96 and the intervening plates 94 towards the partition 91. Thus, pressure is applied to all the containers 96. The flow of liquid reagent from the containers 96 is controlled by pulsing the control valve associated with each container at the frequency appropriate to deliver reagent at the desired rate.

In the examples above, we have described the invention in relation to gas detecting methods using colorimetric techniques. The invention can also be applied to other gas-detecting techniques.

For example the gas absorbed in the cell 15 can be detected by chromatography. An integrated or concentrated sample of gas in liquid is collected by the cell 15 and the solution from the cell is then injected into the gas or liquid chromatographic apparatus.

Other methods for examining the solution from the cell 15 involve replacing the optical cell 22 with other forms of cells which will produce responses in the presence of the gas to be detected. For example a pH is measured using ion selective electrodes, or a conductivity measuring cell may be used in which the electrical conductivity of the liquid between two spaced electrodes is measured

using standard electrical techniques. Spectrophotometric methods may also be used in which the absorbtion of light at particular wavelengths for example UV or IV is measured.

Other possible techniques involve electrochemical oxidation or reduction.

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- 1. A gas analyser comprising a gas absorbing cell having a chamber for liquid separated from a region containing sample gas by a gaspermeable membrane, the chamber having an inlet port for connection to a supply of liquid and an outlet port for connection to sensing apparatus for detecting a change in the liquid due to the presence of the gas to be detected, the effective surface area of the gas-permeable membrane being large compared with the volume of the liquid chamber.
- A gas analyser according to claim 1 in which the ratio of the effective area of the membrane to the volume of the liquid chamber is 5mm⁻¹ or more.
- A gas analyser according to claim 2 in which the ratio is in the range 5 to 20mm⁻¹.
- 4. A gas analyser according to any of claims 1 to 3 in which the liquid chamber has a thickness substantially less than its length and width and the membrane forms one of the major walls of the chamber.
- 5. A gas analyser according to claim 4 in which the thickness of the cell is 0.1mm or less.
- A gas analyser according to any of the preceding claims in which the region containing sample gas communicates with the ambient air.
- 7. A gas analyser according to any of the preceding claims including pumping means in series with the liquid chamber for pumping the liquid through the chamber.
- A gas analyser according to claim 7 in which the pumping means

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comprise non-electric pumping means.

- A gas analyser according to claim 7 or 8 in which the pump delivers liquid at a rate of 5 to 250 1 per minute.
- 10. A gas analyser according to any of the preceding claims in which the liquid is a liquid reagent which undergoes a colour change in the presence of the gas to be detected, and in which the sensing apparatus includes photometric means for detecting the colour change.
- 11. A gas analyser according to any of claims 1 to 10 including means for mixing the liquid with reagents to produce a colour change in the presence of the gas to be detected and in which the sensing apparatus includes photometric means for detecting the colour change.
- 12. A gas analyser according to any of the preceding claims in which the sensing means provides an alarm signal when the level of gas detected exceeds a predetermined value.
- 13. A gas analyser according to any of the preceding claims in which the sensing means includes an optical cell connected to a measuring photometer by an optical fibre.
- 14. A gas analyser according to any of the preceding claims in which the gas permeable membrane comprises a porous plastics material reinforced with a polyester mesh.
- 15. A liquid pump comprising a flexible container containing liquid to be pumped, a pulsed valve in an outlet connected to the flexible container and means for applying pressure to the flexible container.
- 16. A liquid pump according to claim 15 in which the means for applying pressure to the flexible container comprises a spring driven plate.

- 17. A liquid pump according to claim 15 in which the means for applying pressure to the flexible container is air pressure.
- 18. A liquid pump according to claim 17 in which the flexible container is housed in an air-tight housing with an inlet in its wall coupled to a source of compressed gas through a pressure regulator.
- 19. An optical cell comprising a body with a transverse bore closed at its ends by windows, an inlet connected to the bore adjacent one of its ends and an outlet connected to the bore adjacent the other of its ends, the inlet being connected to a source of fluid whereby fluid passes from the inlet to the outlet through the bore, a light source mounted outside one window and a photo detector being mounted outside the other window so that the photo detector detects light from the light source passing through the liquid in the bore.
- 20. An optical cell according to claim 19 in which the light source is a pulsed light source.
- 21. An optical cell according to claim 19 or 20 in which the inlet and outlet to the bore are immediately adjacent the windows and are so arranged that liquid flows into and out of the bore across the inside faces of the windows.
- 22. A gas analyser substantially as hereinbefore described with reference to Figs. 1, 2 or 3 and Figs. 4 and 5 of the accompanying drawings.
- 23. An optical cell substantially as hereinbefore described with reference to Figs. 6 and 7 of the accompanying drawings.
- 24. A pump substantially as hereinbefore described with reference to Fig. 8 of the accompanying drawings.
- 25. A pump substantially as hereinbefore described with reference

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to Fig. 9 of the accompanying drawings.

26. A pump substantially as hereinbefore described with reference to Fig. 10 of the accompanying drawings.

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